A PHYSICAL ORGANIC CHEMIST LOOKS AT HYDROUS PYROLYSIS

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INTRODUCTION. The invention and development of the hydrous pyrolysis technique by Mike Lewan is an important organic geochemical development and a fascinating reaction system.[1] This paper is a consideration of the reactions between kerogens and water which are a key part of hydrous pyrolysis and is based entirely on data from the literature. We begin with a consideration of the nature of water under hydrous pyrolysis conditions. A special concern here will be the question of contact between water and kerogen. The kerogens are three-dimensionally cross-linked-macromolecular systems and as such do not dissolve in water or any other solvent, but solvents can dissolve in the kerogen.[2] Another concern here is the possible mechanisms by which water and kerogens might react.

The solution of pentane or other light hydrocarbons in water is an exothermic process.[3] These insoluble organic molecules have favorable interactions with water. Their insolubility is due to an enormously unfavorable entropy of solution, the familiar hydrophobic effect.[3] As water is heated, its three dimensional hydrogen bonded structure becomes increasingly disarrayed and the entropy driven hydrophobic effect diminishes. The interactions which are responsible for the favorable enthalpy of solution remain so that as water is heated it increasingly becomes a non-polar solvent. This can be seen most easily by looking at the temperature dependence of water's cohesive energy density or its square root, the solubility parameter. These can be calculated as a function of temperature from the data in the Landolt Bornstein Tabellen[4] and equation 1 where δ is the solubility parameter, ΔE_{vap} and ΔH_{vap} are respectively the energy and enthalpy of vaporization, and V_{mole} is the molar volume. Following Regular Solution Theory and its empirical thermodynamically illegitimate extensions, a liquid having the same δ as a polymer will be the best swelling solvent for it.[5] As the two δ values (liquid and polymer) diverge, the sorption of the liquid by the polymer will decrease. The δ value for water decreases from 24 cal$^{1/2}$cm$^{-3/2}$ at temperature to 7.4 cal$^{1/2}$cm$^{-3/2}$ at 360°C, just below the critical temperature. At 350°C, the temperature used in hydrous pyrolysis, the solubility parameter is 9.1 cal$^{1/2}$cm$^{-3/2}$. The solubility for Type I kerogen is approximately 9.75 cal$^{1/2}$cm$^{-3/2}$ and it is expected that the water will dissolve in and have access to all portions of the kerogen under hydrous pyrolysis conditions. It should also swell the kerogen to whatever extent is permitted by the structure of the surrounding rock.

Equation 1

$$\delta = \left(\frac{\Delta E_{vap}}{V_{mole}} \right)^{1/2} = \left(\frac{\Delta H_{vap} - RT}{V_{mole}} \right)^{1/2}$$

While water probably is soluble in kerogen under hydrous pyrolysis conditions, the situation under geological maturation conditions is not as clear. The oil window occurs at much lower temperatures, temperatures at which the solubility parameter for water is so high as to effectively preclude its dissolution in the kerogen at 200°C, the solubility parameter for water is 19 cal$^{1/2}$cm^{-32}. Only if the kerogen is inhomogeneous on the molecular level might water gain access to polar regions. This "first order" consideration of the solubility of water in Type I kerogen raises a concern about using hydrous pyrolysis as a model for geological kerogen maturation. Type II kerogen will probably be similar to Type I.

If temperature were the only variable, the situation would be simple, but we also need to consider pressure effects and salt effects. Lithostatic pressures between 800 bar and 1000 bar are commonly encountered during kerogen maturation.[6] These pressures and the temperatures encountered in petroleum kitchens can have significant effects on the solubility of organic molecules in water.[7] This can be seen most easily in Figure 1 which shows the effect of temperature and pressure on the miscibility of water and 4-methylpiperidine.[7] The addition of salt

can complicate the situation enormously as shown in Figure 2. The situation is sufficiently complicated so that I am unwilling to reach a conclusion as to the solubility of water in kerogen under the conditions existing in petroleum kitchens. This is an important point for understanding not only what is going on in hydrous pyrolysis, but also its use to model kerogen maturation.

The next concern is the mechanisms by which the kerogens and water react. There are three strong indications that this reaction does not occur by radical pathways. As pointed out by Dave Ross, at 330°C β-scission of an alkyl radical is 300 times faster than hydrogen abstraction from water so olefin formation will greatly exceed saturates formation.[8] Formation of large amounts of olefin in hydrous pyrolysis has not to my knowledge been reported and olefins are rare components of crude oils.[6] Lewan has carried out hydrous pyrolysis in the presence of added H_2 and did not observe any significant change in the product distribution.[1] The bond in water at 119.1 kcal/mole is much stronger than the bond in H_2 at 104.2 kcal/mole.[8] A radical that can abstract H from water will abstract H from H_2 much more rapidly so a significant change in the product distribution is expected when hydrogen is added to the hydrous pyrolysis system if it is undergoing a radical reaction with water. The only thing which might affect this would be inaccessibility of hydrogen to the reacting centers and this seems unlikely. Finally, there has been one study of pure compounds under hydrous pyrolysis conditions using simulated oil field brine.[10] n-Hexadecane cracked to give alkanes and olefins in reactions that were inhibited by a radical hydrogen donor. These results are best explained using radical reactions. There was no evidence of hydrogen abstraction from or oxidation by water. These three lines of evidence lead to the conclusion that the reactions between kerogen and water are not occurring by a radical process.

Direct reaction between water and some functional groups is possible, but it is hard to envision hydrocarbon formation from kerogens based solely on water- kerogen reactions of the type so thoroughly studied by Siskin and Katritsky.[11] Both Ross and Helgeson et al have argued for involvement of mineral matter in reactions between organics and water.[12,13] Ross argued for the possibility of a mineral matter catalyzed oxidation of hydrocarbons by water and Helgeson et al argued that in oil reservoirs, hydrocarbons, water, minerals, carboxylic acids and CO_2 had reached thermodynamic equilibrium. In both cases, mineral matter is involved in the oxidation of hydrocarbons by water. This is shown most directly using the scheme below taken directly from a paper by Dave Ross. In it, a hydrocarbon is cleaved and oxidized to CO_2 by a metal oxide, for example an iron oxide which is reduced in the process. In the second step of the reaction, the reduced metal oxide is reoxidized by water generating a pair of hydrogen atoms which are added to an organic molecule. The net reaction is the oxidation of the organic material, kerogen, by water catalyzed by mineral matter. The thermodynamics of this are favorable as long as the end products are carboxylic acids or carbon dioxide. The thermodynamics are not favorable for the formation of intermediate carbon oxidation states such as alcohols or aldehydes. There is some evidence for this chemistry occurring. Eglinton studied the hydrous pyrolysis of several immature kerogens and measured, among other things, the formation of carboxylic acids.[14] The addition of limonite to Kimmeridge kerogen tripled the amount of carboxylic acids formed. The limonite was not altered (XRD analysis). It seems that limonite catalyzes carboxylate formation from Kimmeridge kerogen during hydrous pyrolysis. This is in general agreement with Ross's scheme and Helgeson et al observations.
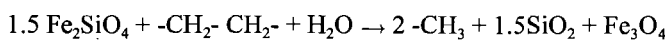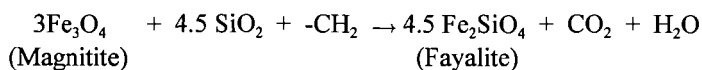
The hydrous pyrolysis reaction system is intriguing both physically and chemically. It is an excellent entree to the chemistry responsible for kerogen maturation and has the advantage that it can be studied in our lifetimes. It is a major step forward and worthy of very careful scrutiny.

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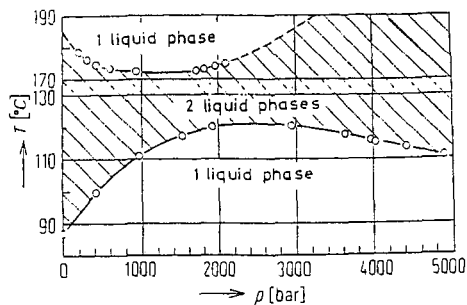
Scheme 1 (from reference 12)

$$3Fe_3O_4 + 4.5\ SiO_2 + -CH_2 \rightarrow 4.5\ Fe_2SiO_4 + CO_2 + H_2O$$
(Magnitite)   (Fayalite)

$$1.5\ Fe_2SiO_4 + -CH_2-CH_2- + H_2O \rightarrow 2\ -CH_3 + 1.5SiO_2 + Fe_3O_4$$

Fig. 1. Pressure influence on liquid-liquid immiscibility in the system 4-methylpiperdine-H$_2$O for χ = const. $\approx \chi_c$ ^{lsct} at 1 bar (from ref. 7).
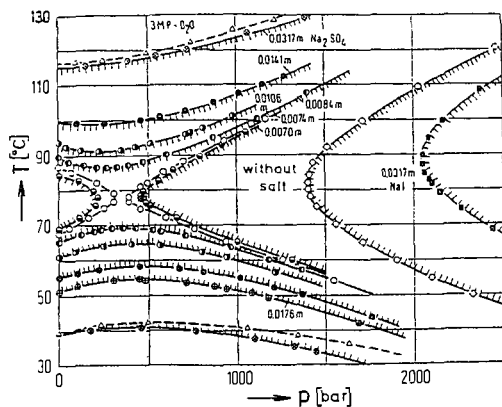

Fig. 2. Salt and pressure effects on liquid-liquid immiscibility in the system 3-methylpyridine-H$_2$O wt.% water/wt% 3-methylpyridine = const. = 7/3; (from ref. 7).